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CHEMICAL SPECIATION STUDIES OF RADIONUCLIDES BY XAFS

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ABSTRACT

The local structures of U(VI) oxide precipitates produced as a function of LiOH concentration have been studied by XAFS. Curve-fitting analyses indicate that the solid formed in 0.1 M LiOH is similar to a schoepite-like phase where distinct linear uranyl groups (UO_2^{2+}) are bridged along the equator by OH ions. At higher LiOH concentrations, the precipitated solids lose their uranyl character and resemble a uranate salt. We have studied the speciation of Tc in cement waste forms, where it is desirable to stabilize the highly soluble form of Tc(VII), TcO_4^- , by *in situ* reduction to a less mobile form, i.e. Tc(IV). Using the XANES to measure the oxidation state, our results show that significant reduction takes place in the presence of the cement additives blast furnace slag (BFS) and Na_2S . In addition, EXAFS data show that *in situ* reduction leads to formation of Tc clusters possessing S and Tc coordination.

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1. INTRODUCTION

Controlling the transport of radionuclides through the environment requires a detailed understanding of the physical factors and processes that determine an element's chemical form or speciation. Such knowledge may be used for predictive purposes or to chemically modify the speciation, thereby changing important properties such as toxicity, or solubility. One of the key issues regarding the disposal of radioactive waste is the concern that over long periods of time, radionuclides may leach out of a given waste form and enter the surrounding environment. Uranium and technetium present examples where there is a strong tendency towards formation of the highly oxidized and soluble species, U(VI)O_2^{2+} and Tc(VII)O_4^- . Uranium, as UO_2^{2+} , will have the propensity to migrate through neighboring aquifers where it can form solid phases which effectively become the secondary source terms. We have previously used XAFS to characterize U precipitates formed in dilute sulfate solutions [1], and in the present study we have extended this work to concentrated LiOH solutions. Leaching of Tc from cement waste forms may be decreased by the use of additives such as blast furnace slag (BFS) which has been proposed to reduce the pertechnetate anion, TcO_4^- , to a less soluble species such as TcO_2 [2]. Herein, XAFS has been used to measure changes in Tc speciation induced by the addition of different chemical additives [3].

2. XAFS DATA ACQUISITION AND ANALYSIS

Uranium L_{III} and Tc K-edge XAFS spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on bending magnet beamline 2-3 using a fully tuned Si (220) double-crystal monochromator. All spectra were collected at room temperature in transmission geometry using argon-filled ionization chambers and a vertical slit of 0.5 mm. Spectra were calibrated with the reference compounds UO_2 (solid) and NH_4TcO_4 (aq), defining the first inflection points as 17166 and 21044 eV, respectively for each reference. XAFS data reduction and non-linear least squares curve-fitting analysis were performed using the programs from EXAFSPAK developed by G. George of SSRL. The theoretical EXAFS modeling code, FEFF6, of Rehr *et al.* [4] was used to calculate the backscattering phases and amplitudes of the individual neighboring atoms. The amplitude reduction factor, S_0^2 , was held fixed at 0.9 for all of the fits. The shift in threshold energy, ΔE_0 , was allowed to vary as a global parameter for all atoms included in the fits (i.e., the same ΔE_0 was used for all shells).

3. URANIUM OXIDE PRECIPITATES

All solutions were prepared using CO_2 -free, deionized water. A stock solution of ^{238}U was made by dissolving uranyl nitrate in concentrated HCl (12 M) and was purified from daughter activities using an anion exchange column. Five precipitation reactions were performed by mixing 0.1 ml of 2.0 M uranyl nitrate (pH=1.0) with 2.0 ml of 0.1, 0.3, 0.5, 1.0, and 5.0 M LiOH stock solutions. The solids precipitated instantly and were recovered as wet pastes (~10 mg each), mixed with BN, and loaded into polyethylene cuvettes for XAFS measurements.

Figure 1 shows the EXAFS data and corresponding Fourier transforms for the precipitated oxides. The EXAFS spectra show good signal-to-noise which extends the useful range of the data out to $k \sim 15 \text{ \AA}^{-1}$. The low- k region is dominated by a low frequency oscillation arising from backscattering of the O atoms in the linear UO_2^{2+} group. This is demonstrated more clearly by the phase-shifted peak at 1.30 Å in the Fourier transforms (FTs). The pattern of FT peaks centered around 1.90 Å in the 0.1 M spectrum is attributed to O atoms lying in the equatorial plane of the UO_2^{2+} ion. Moving from 0.1 to 0.5 M LiOH, a structural transformation is observed as the 1.30 Å peak broadens, shifts to higher R , and the pattern in the equatorial O region is lost. In addition, all of the spectra exhibit a feature(s) at ~3.7 Å, which is assigned to U neighbors. The position of the U peak(s) shifts to lower R upon going from 0.1 to 0.5 M. From 0.5 to 5.0 M LiOH, the structures do not show any significant changes.

Non-linear least squares curve-fitting was done over the range $1\text{--}15 \text{ \AA}^{-1}$ on the raw EXAFS data. The bond lengths and coordination numbers are summarized in Table I. Although these samples may contain a mixture of phases, the structural patterns are easily discerned. The 0.1 M LiOH sample closely resembles the oxide schoepite [1] with ~2 O at 1.81 Å, a split shell of ~5 equatorial O atoms at 2.26 Å and 2.47 Å, and ~2 U at 3.88 Å. As the LiOH concentration increases from 0.1 to 0.3 and 0.5, the axial oxygen bond lengths increase to 1.84 Å and 1.87 Å, respectively, while the equatorial bond lengths decrease. The shell of U atoms becomes split over the range 0.3-5.0 M, with ~2 U at 3.71 Å and ~2 U at 3.92 Å. All of the structural trends observed in the FTs are confirmed by the curve-fitting results.

The normalized U L_{III}-edges are shown in Figure 2. The primary absorption peak at 17.17 keV is associated with an allowed 2p → 6d transition. The shoulder that appears at ca. 17.18 keV has been observed in the L_{III} XANES of numerous U(VI) oxides [6], where it has been proposed to originate from multiple scattering resonances that are associated with the relatively short U-O bond interaction of the uranyl group. This assignment has been confirmed more recently by calculations using FEFF6 [7]. As the axial oxygen bond lengths increase, the position of the MS resonance systematically shifts to lower energy, providing another probe for the structural changes in these precipitated solids.

4. TC IN CEMENT WASTEFORMS

The cement wasteform used in this study consisted of a 1:1 wt% mixture of ordinary Portland cement (OPC) and a simulated waste solution (SWS). The details of the SWS, which is composed of various inorganic salts, have been reported elsewhere [5]. Approximately 1200 ppm of TcO₄⁻ (in the form of a NH₄TcO₄ stock solution) was added to three separate portions of the OPC/SWS mixture. Cement 1 contained only the OPC/SWS mixture, and Cements 2 and 3 were mixed with ~10 wt% of BFS and Na₂S, respectively. The samples were cured in polystyrene UV-visible cuvettes (4 x 10 mm body) for 4 days at 60°C under 100% humidity. Although the edge jumps across the Tc K-edge were less than 0.07, the extreme homogeneity of these solid solutions enabled data to be acquired in transmission mode. (NH₄)₂TcCl₆ solid and NH₄TcO₄ (aq) were measured for comparison.

In Figure 3, we show the Tc K-edge XANES spectra for the Tc cement mixtures and the reference compounds. NH₄TcO₄ displays a prominent 1s → 4d pre-edge transition (dipole forbidden) which becomes more allowed in the noncentrosymmetric, tetrahedral TcO₄⁻ anion. Using this feature as a signature for TcO₄⁻, it is apparent that OPC does not reduce the pertechnetate anion (Cement 1). The presence of BFS in Cement 2 produces partial reduction while the Na₂S in Cement 3 reduces the TcO₄⁻ completely. These results support the contention that reduced leaching in the presence of BFS is due to Tc reduction by constituents in the BFS, i.e., sulfide-containing species [2].

The correspondence in position and the general shape between the XANES of Cement 3 and TcCl₆²⁻ suggests that the Tc species formed in Cement 3 is a Tc(IV) species, possibly possessing a local structure similar to that of TcCl₆²⁻. This is supported by the EXAFS curve-fitting results for Cement 3 shown in Figure 4. The EXAFS spectra for Cement 2 (not shown) and Cement 3 are dominated by a shell of S neighbors at ~2.4 Å. For the BFS-sample, the EXAFS data indicate a residual amount of TcO₄⁻ as observed in the XANES. On the contrary, there is no detectable TcO₄⁻ in the Na₂S-sample, and the EXAFS results give ~ 2 Tc neighbors at 2.80 Å. Addition of Na₂S leads to the formation of a bridged structure similar to that of TcS₂.

5. ACKNOWLEDGMENT

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Table and Figure Captions

- Table I. EXAFS Structural Results for U(VI) Oxide Precipitates
- Figure 1. Uranium L_{III}-edge EXAFS and corresponding Fourier transforms for uranium oxides precipitated in: a) 5.0 M, b) 1.0 M, c) 0.5 M, d) 0.3 M, and e) 0.1 M LiOH.
- Figure 2. Uranium L_{III}-edge XANES spectra of uranium oxides precipitated in: a) 5.0 M, b) 1.0 M, c) 0.5 M, d) 0.3 M, and e) 0.1 M LiOH aqueous solution.
- Figure 3. Technetium K-edge XANES spectra of TcO_4^- , TcCl_6^{2-} , Cement 1 ($\text{TcO}_4^- + \text{OPC}$), Cement 2 ($\text{TcO}_4^- + \text{OPC/BFS}$), and Cement 3 ($\text{TcO}_4^- + \text{OPC/Na}_2\text{S}$).
- Figure 4. Curve fitting deconvolution of Tc K-edge EXAFS and Fourier transforms for Cement 3 illustrating the presence of the Tc-S and Tc-Tc interactions.

Sample	Shell	R(Å)	N	σ^2 (Å ²)
0.1M LiOH	U-O _{ax}	1.81	2.0	0.0018
	U-O _{eq1}	2.26	2.7	0.0066
	U-O _{eq2}	2.47	2.0	0.0059
	U-U	3.88	2.2	0.0052
0.3M LiOH	U-O _{ax}	1.84	2.0	0.0028
	U-O _{eq1}	2.26	3.4	0.0060
	U-O _{eq2}	2.47	1.8	0.0139
	U-U	3.70	1.4	0.0062
	U-U	3.92	2.4	0.0088
0.5M LiOH	U-O _{ax}	1.87	2.0	0.0021
	U-O _{eq1}	2.25	4.5	0.0086
	U-U	3.71	2.0	0.0057
	U-U	4.20	2.3	0.0116
1.0M LiOH	U-O _{ax}	1.87	2.0	0.0023
	U-O _{eq1}	2.26	4.1	0.0083
	U-U	3.72	2.3	0.0074
	U-U	4.22	2.0	0.0116
5.0M LiOH	U-O _{ax}	1.87	2.0	0.0019
	U-O _{eq1}	2.26	4.4	0.0081
	U-U	3.72	2.5	0.0080
	U-U	4.20	1.7	0.0105

Table I P. G. Allen et al.

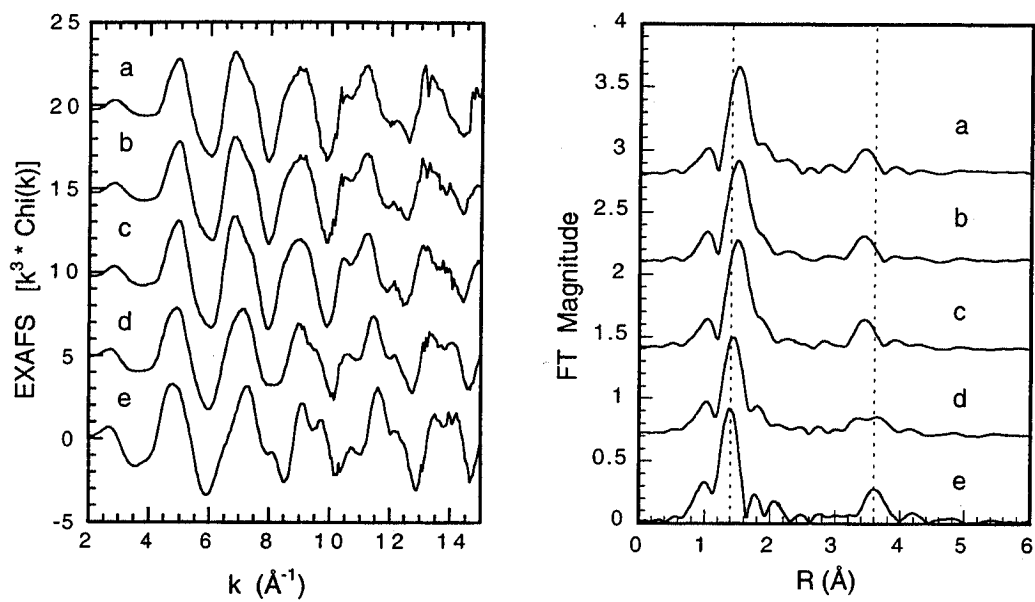


Figure 1

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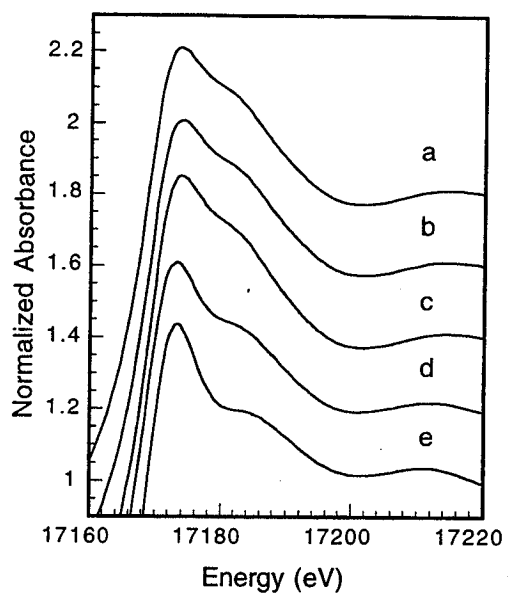


Figure 2

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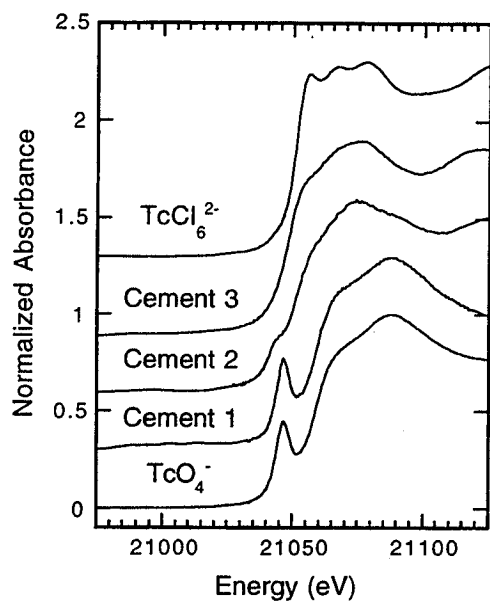


Figure 3

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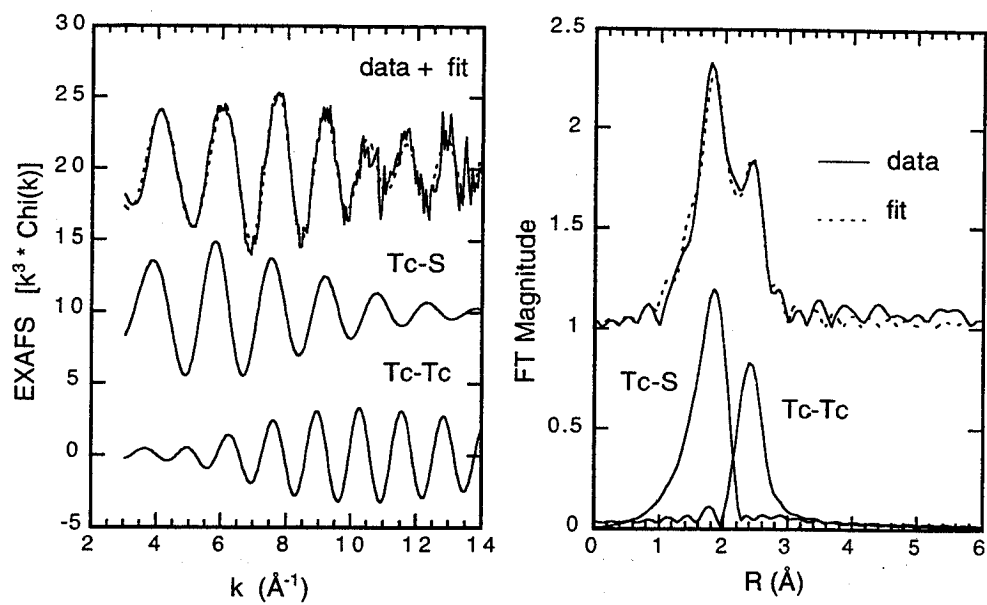


Figure 4

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